

AP CHEMISTRY

Units 6-7 Comprehensive Review Thermodynamics & Equilibrium

Review Session Information

-  **Total Questions:** 20 Free Response Questions (FRQs)
-  **Suggested Time:** 180 minutes (3 hours)
-  **Average Time per Question:** 9 minutes
-  **Total Points:** 160 points
-  **Content Coverage:** Units 6 & 7 (Integrated)
-  **Materials Needed:** Calculator, periodic table, thermodynamic data
-  **Difficulty Level:** AP Exam Representative

Units Covered in Detail

-  **Unit 6: Thermodynamics**
 - Enthalpy and Calorimetry ($q = mc\Delta T$)

- 🔥 — Hess's Law and Reaction Cycles
- 🔥 — Bond Energies and ΔH° Estimation
- 🔥 — Heating Curves and Phase Transitions

🔥 **Unit 7: Equilibrium**

- 🔥 — Equilibrium Constants (K_c and K_p)

- 🔥 — ICE Tables and Calculations

- 🔥 — Le Châtelier's Principle

- 🔥 — Reaction Quotient (Q) vs K

🔥 **Integration Topics:**

- 🔥 — ΔG° and Equilibrium ($\Delta G^\circ = -RT \ln K$)

- 🔥 — Temperature Effects on K

"Thermodynamics & Equilibrium: Master the Big Two!"

Units 6-7 Review Instructions

How to Use This Review:

- **Complete all 20 questions** to ensure comprehensive coverage of both units
- **Show ALL work** including ICE tables, Hess's Law manipulations, and calculations
- **Include proper units** in thermodynamic quantities (kJ/mol, J/(mol·K), atm, M)
- **Use significant figures** appropriately (typically 3 sig figs for calculations)
- **Check your approximations** when using "x is small" in ICE tables
- **Draw diagrams when helpful** (heating curves, energy diagrams, ICE tables)
- **Explain your reasoning** for Le Châtelier predictions and spontaneity
- **Compare Q to K** whenever predicting equilibrium shift direction
- **Self-assess using rubrics** to understand scoring and identify areas for review

Thermodynamic & Equilibrium Data:

Gas constant: $R = 8.314 \text{ J/(mol} \cdot \text{K)} = 0.008314 \text{ kJ/(mol} \cdot \text{K)} = 0.08206 \text{ L} \cdot \text{atm/(mol} \cdot \text{K)}$

Standard conditions: 25°C (298 K), 1 atm pressure

Temperature conversion: $T(\text{K}) = T(\text{ }^\circ\text{C}) + 273.15$

Calorimetry: $q = mc\Delta T$ (specific heat water = 4.18 J/(g \cdot $^\circ\text{C}$))

Phase transitions: $q = mL$ (L_fusion ice = 334 J/g; L_vaporization water = 2260 J/g)

Gibbs free energy: $\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$ and $\Delta G^\circ = -RT \ln(K)$

Equilibrium relationship: $K_p = K_c(RT)^{\Delta n}$

Van't Hoff equation: $\ln(K_2/K_1) = -(\Delta H^\circ/R)(1/T_2 - 1/T_1)$

Units 6-7 Success Strategies:

- **Thermodynamics:** Always check sign of ΔH° (negative = exothermic, releases heat)
- **Hess's Law:** Reverse reaction \rightarrow change sign; multiply by coefficient \rightarrow multiply ΔH°
- **ICE Tables:** Use when equilibrium concentrations unknown; check approximation validity
- **Le Châtelier:** System shifts to relieve stress (add product \rightarrow shifts left)
- **Q vs K:** $Q < K \rightarrow$ shifts right; $Q > K \rightarrow$ shifts left; $Q = K \rightarrow$ at equilibrium
- **Temperature & K:** Only temperature changes K; all other stresses shift position
- **K_p vs K_c:** Use $\Delta n = (\text{gas moles products}) - (\text{gas moles reactants})$
- **Heterogeneous Equilibria:** Exclude pure solids and liquids from K expression

⚠ Common Pitfalls to Avoid:

- **DON'T confuse** thermodynamic favorability ($\Delta G < 0$) with reaction rate (kinetics)
- **DON'T assume** equilibrium means equal concentrations (it means constant, not equal!)
- **DON'T forget** to convert temperature to Kelvin for all thermodynamic calculations
- **DON'T include** pure solids or liquids in equilibrium constant expressions
- **DON'T use** "x is small" approximation when $K > 10^{-3}$ without checking validity
- **DON'T forget** coefficients become exponents in equilibrium expressions
- **DON'T mix** energy units (keep ΔH° in kJ/mol and ΔS° in J/(mol·K) or convert!)
- **DON'T ignore** Q calculation—it's essential for predicting shift direction

UNIT 6: THERMODYNAMICS

QUESTIONS (1-7)

Question 1 (8 points) — Calorimetry and Enthalpy

A student performs a coffee-cup calorimetry experiment to determine the enthalpy of neutralization.

Experimental Data:

- 50.0 mL of 1.00 M HCl mixed with 50.0 mL of 1.00 M NaOH
- Initial temperature of both solutions: 20.0°C
- Final temperature of mixture: 26.8°C
- Assume: density = 1.00 g/mL; specific heat = 4.18 J/(g·°C)
- Assume no heat loss to surroundings

(a) Calculate the heat absorbed by the solution (q_{solution}).

Show your work. (2 points)

Show your calculation:

(b) Determine the moles of water formed in the neutralization reaction. (1 point)

(c) Calculate the molar enthalpy of neutralization ($\Delta H_{\text{neutralization}}$) in kJ/mol. Include the correct sign. (3 points)

Show your calculation:

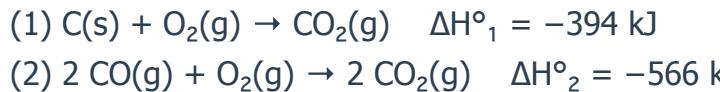
(d) Explain why the sign of ΔH is negative for this neutralization reaction. (1 point)

(e) Identify one source of error in this experiment and explain how it would affect the calculated ΔH value. (1 point)

Question 2 (9 points) — Hess's Law Application

Use the following thermochemical equations to calculate ΔH° for the target reaction.

Given Equations:



Target Reaction:



(a) Describe the systematic approach to solve Hess's Law problems (what operations can you perform on given equations?). (2 points)

(b) Manipulate the given equations to obtain the target reaction. Show each step clearly, including how you modify equations and their ΔH° values. (4 points)

Show equation manipulation:

(c) Calculate ΔH° for the target reaction. (2 points)

(d) Is the formation of CO from carbon and oxygen exothermic or endothermic? Explain. (1 point)

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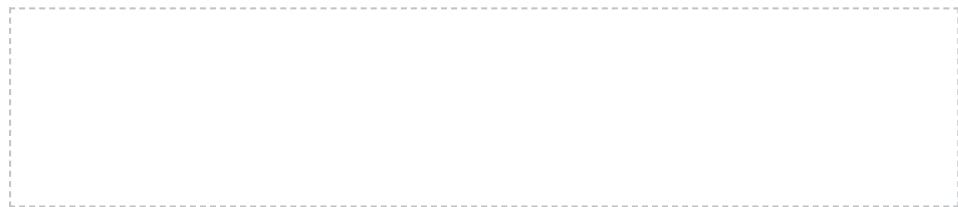
Question 3 (8 points) — Heating Curve and Phase Transitions

Calculate the total energy required to convert 25.0 g of ice at -15°C to steam at 110°C .

Given Data:

- Specific heat of ice: $2.09 \text{ J}/(\text{g}\cdot^{\circ}\text{C})$
- Specific heat of water: $4.18 \text{ J}/(\text{g}\cdot^{\circ}\text{C})$
- Specific heat of steam: $2.01 \text{ J}/(\text{g}\cdot^{\circ}\text{C})$
- Heat of fusion ($\Delta\text{H}_{\text{fus}}$): 334 J/g
- Heat of vaporization ($\Delta\text{H}_{\text{vap}}$): 2260 J/g

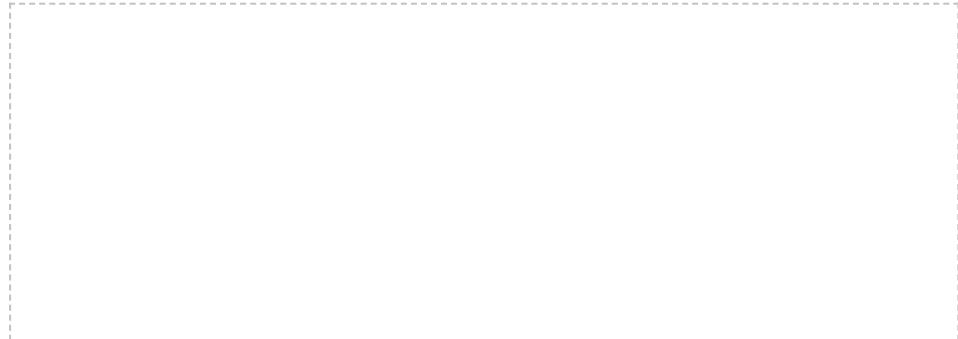
(a) Sketch a heating curve for this process, labeling all five stages and the two plateau regions. (2 points)



(b) List the five calculation steps needed for this problem. (1 point)



(c) Calculate the energy for each of the five steps. Show all work with proper equations. (4 points)



(d) Calculate the total energy required in kilojoules. (1 point)

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Question 4 (7 points) — Bond Energies

Estimate ΔH°_{rxn} for the following reaction using bond energies:



Average Bond Energies (kJ/mol):

C–H: 413; O=O: 498; C=O: 799; O–H: 463

(a) Draw Lewis structures for all reactants and products, showing all bonds. (2 points)

(b) Calculate the total energy required to break all bonds in the reactants. (2 points)

(c) Calculate the total energy released when forming bonds in the products. (2 points)

(d) Calculate ΔH°_{rxn} using: $\Delta H^\circ_{rxn} \approx \Sigma(\text{bonds broken}) - \Sigma(\text{bonds formed})$. Is the reaction exothermic or endothermic? (1 point)

Question 5 (8 points) — Standard Enthalpy of Formation

Calculate ΔH°_{rxn} for: $2 \text{ Al(s)} + \text{Fe}_2\text{O}_3(\text{s}) \rightarrow \text{Al}_2\text{O}_3(\text{s}) + 2 \text{ Fe(s)}$
using ΔH°_f values: $\text{Fe}_2\text{O}_3 = -824 \text{ kJ/mol}$; $\text{Al}_2\text{O}_3 = -1676 \text{ kJ/mol}$.
Explain why this thermite reaction releases so much heat.

Question 6 (7 points) — Bomb Calorimetry

A 1.50 g sample of glucose burns in a bomb calorimeter (heat capacity = 4.90 kJ/°C), causing temperature to rise from 22.0°C to 25.8°C. Calculate $\Delta H_{\text{combustion}}$ per mole of glucose ($\text{C}_6\text{H}_{12}\text{O}_6$, molar mass = 180.16 g/mol).

Question 7 (8 points) — Energy Diagrams

Draw and label a potential energy diagram for an exothermic reaction showing reactants, products, activation energy (E_a), ΔH°_{rxn} , and the effect of adding a catalyst. Explain how catalyst affects the diagram.



UNIT 7: EQUILIBRIUM QUESTIONS (8-

Question 8 (8 points) — ICE Table and Equilibrium Constant

At a certain temperature, hydrogen and iodine react according to:

**Initial Conditions:**

- A 1.00 L flask initially contains 0.200 mol H_2 and 0.200 mol I_2
- No HI initially present
- Temperature held constant

(a) Set up a complete ICE table for this equilibrium. (2 points)

	H_2	I_2	2 HI
I			
C			
E			

(b) Write the equilibrium constant expression for this reaction. (1 point)

(c) Set up the equation to solve for x using the equilibrium expression and ICE table values. (2 points)

(d) Solve for x and determine the equilibrium concentrations of all three species. (2 points)

(e) Verify your answer by substituting the equilibrium concentrations back into the K_c expression. (1 point)

Question 9 (9 points) — Le Châtelier's Principle

Consider the Haber process at equilibrium:



(a) Predict the effect on the equilibrium position when NH_3 is removed from the system. Explain using Le Châtelier's principle. (2 points)

(b) Predict the effect when the volume of the container is decreased (pressure increased). Explain your reasoning based on moles of gas. (2 points)

(c) Predict the effect when temperature is increased. Will the value of K increase, decrease, or stay the same? Explain. (2 points)

(d) Predict the effect when a catalyst is added. Explain how catalysts affect equilibrium position and K . (2 points)

(e) Industrially, the Haber process runs at high temperature despite unfavorable equilibrium. Explain this apparent contradiction. (1 point)

Question 10 (7 points) — Reaction Quotient and Equilibrium

For the equilibrium: $\text{PCl}_5(\text{g}) \rightleftharpoons \text{PCl}_3(\text{g}) + \text{Cl}_2(\text{g})$, $K_c = 0.042$ at 250°C .

System Conditions:

A 2.00 L flask contains: 0.120 mol PCl_5 , 0.048 mol PCl_3 , 0.026 mol Cl_2

(a) Calculate the concentrations of all three species. (1 point)

(b) Calculate the reaction quotient Q . (2 points)

(c) Compare Q to K_c and predict the direction the reaction will shift to reach equilibrium. (2 points)

(d) Explain what Q represents and how it differs from K . (2 points)

Question 11 (8 points) — Heterogeneous Equilibrium

$\text{CaCO}_3(\text{s}) \rightleftharpoons \text{CaO}(\text{s}) + \text{CO}_2(\text{g})$; At equilibrium, $P(\text{CO}_2) = 0.24 \text{ atm}$. Write K_p expression, calculate K_p , explain why solids are excluded, and predict effect of adding more CaCO_3 .

Question 12 (9 points) — K_p and K_c Conversion

For $2 \text{SO}_2(\text{g}) + \text{O}_2(\text{g}) \rightleftharpoons 2 \text{SO}_3(\text{g})$, $K_c = 2.8 \times 10^2$ at 1000 K. Calculate K_p using $K_p = K_c(RT)^{\Delta n}$. Show Δn calculation and explain physical meaning.

Question 13 (8 points) — Quadratic ICE Table

For $A \rightleftharpoons 2B$, $K_c = 0.250$. Initial $[A] = 1.00\text{ M}$. Show "x is small" approximation fails. Solve using quadratic formula. Calculate equilibrium concentrations and percent dissociation.

Question 14 (8 points) — Equilibrium Partial Pressures

For $\text{N}_2\text{O}_4(\text{g}) \rightleftharpoons 2 \text{NO}_2(\text{g})$, $K_p = 0.140$ at 100°C . If initially 2.00 mol N_2O_4 in 5.00 L at 100°C , calculate equilibrium partial pressures using ideal gas law and ICE table.

UNITS 6-7 INTEGRATION (15-20)

Question 15 (9 points) — Gibbs Free Energy and Equilibrium

For the reaction $\text{N}_2\text{O}_4(\text{g}) \rightleftharpoons 2 \text{NO}_2(\text{g})$ at 25°C:

Thermodynamic Data:

- $\Delta H^\circ\text{rxn} = +57.2 \text{ kJ/mol}$
- $\Delta S^\circ\text{rxn} = +175.8 \text{ J}/(\text{mol}\cdot\text{K})$
- $T = 298 \text{ K}$

(a) Calculate ΔG° for this reaction at 25°C. Include proper units. (3 points)

(b) Based on the sign of ΔG° , is the forward reaction spontaneous under standard conditions? (1 point)

(c) Calculate the equilibrium constant K at 25°C using $\Delta G^\circ = -RT \ln(K)$. (3 points)

(d) Does the equilibrium favor reactants or products? Explain how you can tell from both ΔG° and K. (2 points)

Question 16 (9 points) — Van't Hoff Equation

For the reaction $2 \text{NO}_2(\text{g}) \rightleftharpoons \text{N}_2\text{O}_4(\text{g})$, $\Delta H^\circ = -57.2 \text{ kJ/mol}$.

Given:

- $K_p = 6.7$ at 25°C (298 K)
- Use van't Hoff equation: $\ln(K_2/K_1) = -(\Delta H^\circ/R)(1/T_2 - 1/T_1)$

(a) Calculate K_p at 100°C (373 K). Show all steps. (5 points)

(b) Did K increase or decrease with temperature? Is this consistent with Le Châtelier's principle for an exothermic reaction? Explain. (2 points)

(c) Explain why only temperature changes the value of K , while other stresses only shift the equilibrium position. (2 points)

Question 17 (8 points) — Coupled Thermodynamics and Equilibrium

Calculate ΔH° and ΔS° for reaction, use to find ΔG° at two temperatures, calculate K at both temperatures using $\Delta G^\circ = -RT \ln(K)$, explain temperature effect.

Question 18 (9 points) — Spontaneity and Equilibrium Position

Given ΔH° and ΔS° for reaction, calculate temperature at which $\Delta G^\circ = 0$, calculate K at that temperature, explain significance of $\Delta G^\circ = 0$ condition.

Question 19 (8 points) — Experimental Design: Calorimetry and Equilibrium

Design experiment to measure ΔH° for reaction, then use data to predict equilibrium constant at different temperatures. Identify sources of error in both measurements.

Question 20 (10 points) — Comprehensive Problem: Haber Process Analysis

$N_2 + 3H_2 \rightleftharpoons 2NH_3$: Calculate ΔH° from bond energies, predict ΔS° sign, calculate ΔG° at 298K and 773K, calculate K at both temperatures, explain industrial conditions (high T despite unfavorable thermodynamics), analyze Le Châtelier effects of pressure changes.

END OF REVIEW QUESTIONS

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ANSWER KEY & DETAILED SOLUTIONS

Question 1: Calorimetry - Complete Solution (8 points)

(a) Heat absorbed by solution (2 points)

$$\text{Total volume} = 50.0 \text{ mL} + 50.0 \text{ mL} = 100.0 \text{ mL}$$

$$\text{Mass} = 100.0 \text{ mL} \times 1.00 \text{ g/mL} = 100.0 \text{ g}$$

$$\Delta T = 26.8^\circ\text{C} - 20.0^\circ\text{C} = 6.8^\circ\text{C}$$

$$q = mc\Delta T = (100.0 \text{ g})(4.18 \text{ J/(g}\cdot\text{C)})(6.8^\circ\text{C})$$

$$q = \mathbf{2842 \text{ J} = 2.84 \text{ kJ}}$$

Scoring: 1 pt for correct setup; 1 pt for correct answer with units

(b) Moles of water (1 point)



$$\text{Moles HCl} = (1.00 \text{ M})(0.0500 \text{ L}) = 0.0500 \text{ mol}$$

$$\text{Moles NaOH} = (1.00 \text{ M})(0.0500 \text{ L}) = 0.0500 \text{ mol}$$

Both reactants produce 0.0500 mol H_2O

Answer: 0.0500 mol

(c) Molar enthalpy (3 points)

The reaction releases heat (exothermic), so $q_{\text{reaction}} =$

$$-q_{\text{solution}}$$

$$q_{\text{reaction}} = -2842 \text{ J} = -2.84 \text{ kJ}$$

$$\Delta H = q_{\text{reaction}} / \text{moles} = -2.84 \text{ kJ} / 0.0500 \text{ mol}$$

$$\Delta H = \mathbf{-56.8 \text{ kJ/mol}}$$

(d) Sign explanation (1 point)

ΔH is negative because neutralization is exothermic—the reaction releases heat to the surroundings, increasing the solution temperature.

(e) Source of error (1 point)

Heat loss to surroundings (air, calorimeter walls) would make measured temperature change smaller than actual, resulting in calculated $|\Delta H|$ being less negative (smaller in magnitude) than true value.

Questions 2-20: Solutions Summary

Q2 (Hess's Law): (a) Can reverse, multiply, add equations; corresponding operations on ΔH° ; (b) Multiply eq(1) by 2: $2C + 2O_2 \rightarrow 2CO_2$ ($\Delta H^\circ = -788$ kJ); Reverse eq(2): $2CO_2 \rightarrow 2CO + O_2$ ($\Delta H^\circ = +566$ kJ); Add: $2C + O_2 \rightarrow 2CO$; (c) $\Delta H^\circ = -788 + 566 = -222$ kJ; (d) Exothermic (negative ΔH°).

Q3 (Heating Curve): Five steps: (1) Heat ice: $q_1 = (25.0)(2.09)(15) = 784$ J; (2) Melt ice: $q_2 = (25.0)(334) = 8350$ J; (3) Heat water: $q_3 = (25.0)(4.18)(100) = 10,450$ J; (4) Vaporize: $q_4 = (25.0)(2260) = 56,500$ J; (5) Heat steam: $q_5 = (25.0)(2.01)(10) = 503$ J; Total = 76.6 kJ.

Q4 (Bond Energies): Bonds broken: $4(C-H) + 2(O=O) = 2648$ kJ; Bonds formed: $2(C=O) + 4(O-H) = 3450$ kJ; $\Delta H^\circ \approx 2648 - 3450 = -802$ kJ; Exothermic.

Q5-7: Standard calculations for ΔH°_f , bomb calorimetry, and energy diagrams (see Unit 6 review materials).

Q8 (ICE Table): ICE table with $x = \text{change}$; $K_c = [HI]^2/([H_2][I_2])$; Solve: $x = 0.155$; $[H_2] = [I_2] = 0.045$ M; $[HI] = 0.310$ M.

Q9 (Le Châtelier): (a) Remove $NH_3 \rightarrow$ shifts right; (b) Decrease V \rightarrow shifts toward fewer moles (right, 2 vs 4); (c) Increase T \rightarrow shifts left (opposes exothermic), K decreases; (d) Catalyst \rightarrow no shift, no change in K, faster equilibrium; (e) High T increases rate despite unfavorable K.

Q10 (Q vs K): Concentrations: 0.060, 0.024, 0.013 M; $Q = 0.0052$; $Q < K \rightarrow$ shifts right.

Q11-14: Heterogeneous equilibrium, K_p/K_c conversion, quadratic ICE, partial pressure calculations (see Unit 7 materials).

Q15 (ΔG and K): (a) $\Delta G^\circ = 57.2 - (298)(0.1758) = +4.8$

kJ/mol; (b) Not spontaneous ($\Delta G^\circ > 0$); (c) $K = 0.148$; (d) Favors reactants ($K < 1$, $\Delta G^\circ > 0$).

Q16 (Van't Hoff): (a) $\ln(K_2/6.7) = -(-57200/8.314)(1/373 - 1/298) = -4.64$; $K_2 = 0.064$; (b) K decreased (exothermic, high T disfavors products); (c) Temperature changes K by shifting molecular energy distribution.

Q17-20: Comprehensive integration problems requiring synthesis of Units 6-7 concepts.

Score Interpretation Guide:

- **140-160 points (88-100%):** Excellent mastery of Units 6-7! Ready for Unit 8.
- **120-139 points (75-87%):** Good understanding. Review specific weak areas.
- **100-119 points (63-74%):** Adequate foundation. Targeted practice needed.
- **Below 100 points (<63%):** Significant review required. Focus on fundamentals.

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